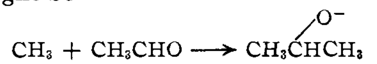
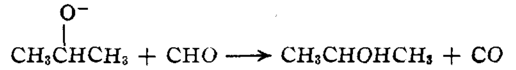
explain formation of di-*n*-propylcarbinol in the peroxide catalyzed decomposition of *n*-butyraldehyde could offer a possible explanation of these discrepancies. For acetaldehyde a typical mechanism might be



$$CH_3 + CH_3CHO \longrightarrow CH_3\overset{O^-}{C}HCH_3 \qquad (7)$$



$$CH_3\overset{O^-}{C}HCH_3 + CHO \longrightarrow CH_3CHOHCH_3 + CO \qquad (8)$$

Evidence for the existence of such a decomposition sequence would rest on the identification of isopropyl alcohol in the condensable products. Qualitative mass spectrometric investigation gave some evidence of the presence of isopropyl alcohol and acetone, possibly as a consequence of methyl and acetyl combination, but positive identification was difficult because of screening of the spectra of these compounds by aldehyde polymer fractions. The approach of the methane/carbon monoxide ratio to unity at shorter wave lengths and higher temperatures may well be attributed to instability of the condensed methyl–acetaldehyde radical formed in reaction (7) and its dissociation into methane and an acetyl radical.

Acknowledgment.—The mass spectrometer used for analytical purposes in these studies was a gift to the University of California, Los Angeles, by the Signal Oil and Gas Co., of Los Angeles. During the period of study the second-named author was holder of the H. M. Mosher Fellowship established by this same company. The research project of which this study was a part, has received financial aid from the Research Corporation, New York.

Summary

The photochemical behavior of a mixture of acetaldehyde and acetaldehyde-*d* has been investigated from 30 to 250° in the wave length region 3130 to 2380 Å. The variation in the ratio of methane-*d* to methane (CH_3D/CH_4) was studied in detail. The amount of CH_4 formed under all conditions was relatively much higher than would be predicted from the composition of the aldehyde mixture if analogous reactions involving similar species containing hydrogen or deuterium atoms had equal velocities. The ratio of CH_3D/CH_4 at 30° varied from 0.63 at 3130 Å. to 1.46 at 2380 Å. and at 250° from 1.19 at 3130 Å. to 1.15 at 2380 Å.

The probability of various type chain mechanisms involving the methyl radical have been discussed. On the basis of experimental evidence no definite choice could be made between a mechanism involving the capture of the acyl hydrogen atoms of acetaldehyde molecules by methyl radicals and one by which the methyl hydrogen atoms were removed from the parent molecules. The presence of appreciable ethane-*d* and ethane-d_2 in the products may be regarded as some evidence in favor of the methyl hydrogen capture mechanism. Evidence is presented which indicates that both mechanisms were not operating simultaneously.

The distribution of H and D in the hydrogen formed during photolysis is greatly different from the distribution in the original aldehyde mixture. Hydrogen is evidently formed mainly from the acyl part of the acetaldehyde molecule.

The excess of carbon monoxide over methane in photolyses at 30° and long wave lengths necessitates the existence of some type of condensation reaction for methyl radicals. The removal of methyl radicals by combination with acetaldehyde molecules to give a condensed radical and subsequent combination of this radical with formyl radicals to yield carbon monoxide and isopropyl alcohol may be a possible explanation.

Los Angeles, Calif. Received January 24, 1950

[From the Kodak Research Laboratories, Communication No. 1318]

The Use of the Stationary Platinum Microelectrode in the Determination of Half-Wave Potentials

By D. B. Julian and W. R. Ruby

In the polarographic study of the oxidation–reduction potentials of some substituted *p*-phenylenediamines used as photographic developers, certain limitations of the dropping mercury electrode precluded its use. For this reason, an investigation was made of the behavior of the platinum microelectrode as the polarizing electrode in the determination of half-wave potentials. The application of solid metal microelectrodes to polarographic determinations has been investigated by a number of workers.[1–6]

A careful and extensive investigation by Laitinen and Kolthoff[1] of the stationary platinum electrode has shown that a steady state is obtained, if one waits for several minutes after applying each increase in voltage. Based upon this work and

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(1) H. A. Laitinen and I. M. Kolthoff, This Journal, **61**, 3344 (1939).

(2) O. H. Müller, *ibid.*, **69**, 2992 (1947).

(3) S. I. Sinyakova, *Trudy Vsesoyuz Konferentii Anal. Khim.* (Proceedings of the All-Union Conference of Analytical Chemistry), **2**, 529 (1943).

(4) E. M. Skobets, L. S. Berenblum and N. N. Atamanenko, *Zavodskaya Laboratoriya* (*U.S.S.R.*), **14**, 131, No. 2 (1948).

(5) S. D. Miller, *Trudy Vsesoyuz Konferentii Anal. Khim.*, **2**, 551 (1943).

(6) Yu. S. Lyalikov and V. I. Karmazin, *Zavodskaya Laboratoriya* (*U.S.S.R.*), **14**, 138, No. 2 (1948).

preliminary experiments of our own, we evolved a technique using the platinum microelectrode which has proved satisfactory for the limited field in which it has been used.

The factors most pertinent to the successful use of the platinum microelectrode for determinations using automatic equipment appear to be: (1) the use of small rate of change of applied voltage, *e. g.*, 20 to 40 millivolts per minute, (2) the elimination of vibrational and thermal disturbances of the diffusion layer, (3) the use of a reference electrode and potentiometer for measurement of the actual potential of the microelectrode, and (4) the design of the microelectrode itself, which assures freedom of diffusion to and from the surface. In view of these and other less important factors, we shall describe in some detail the apparatus and method used in our work.

Experimental

Apparatus.—Although a simple manual type of apparatus could be used for this type of work, the use of automatic equipment for the application of the small increments of voltage and for recording the resulting diffusion current results in considerable saving in operator time. The polarograph which was assembled and used for this work consists of four major components: (1) a motor-driven slidewire with accessory controls, (2) a current-measuring system consisting of a sensitive galvanometer and a suitable control circuit, (3) a pen recording-unit for recording diffusion current as a function of applied voltage, and (4) an accurate potentiometer to measure the actual e. m. f. of the electrode at appropriate intervals.

The slidewire has a resistance of 10 ohms covered in 10 turns, in either 10, 20, or 40 minutes as desired, and is connected to give a continuously changing voltage over any selected range of anodic and/or cathodic polarization in the manner described by Lykken, Pompeo and Weaver.[7] A set of accurately positioned contact points closes a marker circuit to give reference "pips" on the recorder chart and a flash signal at the external potentiometer. The galvanometer has a sensitivity of 10^{-8} amp./mm./meter, a period of fourteen seconds, and an internal resistance of 1200 ohms. The "compensated" Ayrton shunt covers a range of 1 to 10,000 in 21 equal steps and by stepwise compensation maintains an external resistance of 2800 ohms. The pen recording-unit is similar to one described by Pompeo and Penther,[8] with modifications suggested by Williams and Hood.[9] The modifications included the modulation of the galvanometer light beam and using an a.-c. amplifier to avoid interference from room lighting. The pen movement is proportional to the galvanometer deflection, and the chart movement is integrated with the slidewire motor drive. The resulting chart recording is thus diffusion current *vs.* applied voltage. A Leeds and Northrup Type K Potentiometer is used to measure the necessary electrode potentials and for calibration of the galvanometer-recorder system.

The reaction cell and electrode system is designed to reduce to a minimum those factors which interfere with the successful use of the stationary microelectrode. The system has a low internal resistance to the applied voltage when saturated bridge solutions are used (< 700 ohms). The non-polarizing electrode and the reference electrode are separated to secure a reliable reference potential at high current values. The reaction vessel and the reference calomel electrode are thermostated at 25° to prevent thermal diffusion in the former and to ensure constant temperature in both during potential measurements. Noticeable thermal effects at the electrodes were encountered only when the solution temperature was 10° or more different from its surroundings. The use of an agar plug in the bridge tip and the position of the bridge tip in the reaction cell relative to the stationary electrode are important to minimize the effects of streaming from the bridge solution. The entire system is so mounted as to reduce vibration effects to a minimum. No quantitative study of the effect of vibrational and thermal disturbances has been made, but the following observations have been made. Vibrations from an exhaust fan which are perceptible to the hand caused erratic deflections of the galvanometer. The use of antivibration rubber mounts (Lord Mfg. Co.), overloaded by 50% with a 50-pound cast-iron base as an electrode support, eliminated the difficulty, even for small-diameter electrodes (7 mil), where the disturbances were most pronounced.

Well-annealed bright platinum wire is used for the polarizing electrode. Wire, in diameters of 7, 10, 15, 20 and 30 mils, varying in length from 2 to 6 millimeters, has been used successfully. For a 5×10^{-4} molar concentration of a *p*-phenylenediamine, we have found a 15-mil wire having an exposed length of about 5 millimeters to be most satisfactory. A thin Pyrex glass sleeve is first sealed onto the wire and then sealed into a larger glass tube bent at right angles, leaving from 3 to 5 millimeters of the sleeve extending beyond the larger tube. At higher diffusion currents, the use of an electrode extending at right angles to its support gives some improvement in stability as compared to an electrode extending downward from its support.

Materials.—Analytical Grade inorganic chemicals were used in the preparation of buffer and bridge solutions. The N,N-diethylglycine used as a buffer salt was prepared by C. F. H. Allen, of these Laboratories. A. Weissberger, J. R. Thirtle and R. L. Bent, of these Laboratories, prepared the various substituted *p*-phenylenediamines in a high degree of purity and also purified the hydroquinone, quinone, and *p*-aminophenol used. The mercury used for the dropping mercury electrode and in the preparation of the calomel half-cells was "thermometer grade," obtained from the Taylor Instrument Company. The calomel was of the commercial grade especially prepared for calomel electrodes.

Buffer solutions were made by standard procedures using distilled water. The values for the *p*H of the buffers and of the solutions were determined by means of a Beckman Model G *p*H Meter. The accuracy of these values is better than ±0.04 unit.

Method.—The galvanometer–recorder system employed was calibrated by shorting the cell terminals and applying the required voltage to obtain a given unit of deflection of the recording pen, then measuring the potential across a standard resistance. By this method the microamperes per unit of deflection can be calculated. Current–voltage curves were determined for the buffer solutions, and, where significant, were used in applying corrections to the curves obtained from the solutions under test. Before the addition of a weighed sample of developing agent or other material under test, the buffer solution was freed of oxygen by bubbling with special "lamp-grade" nitrogen, obtained from the Linde Company. After the solution had been placed in the cell, it was subjected to further bubbling, and was kept under a blanket of nitrogen flowing over the top of the solution during the determination. A pair of platinum electrodes are usually used for each solution, a current-voltage curve being obtained for each, the two curves serving as a check on each other. A minimum of four current–voltage curves is usually necessary to allow for suitable evaluation of the half-wave potential. Before use, the electrodes are cleaned first in concentrated nitric acid, washed, then cleaned in chromic acid, and finally thoroughly washed in distilled water. They are placed in the cell before the final bubbling with nitrogen.

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(7) L. Lykken, D. J. Pompeo and J. R. Weaver, *Ind. Eng. Chem., Anal. Ed.*, **17**, 724 (1945).

(8) D. J. Pompeo and C. J. Penther, *Rev. Sci. Inst.*, **13**, 218-222 (1942).

(9) Van Zandt Williams, Perkins-Elmer Company, Glenbrook, Conn., and R. L. Hood, American Optical Company, Stamford, Conn., private communication.

Tests have shown that the rate of applying voltage can be varied over rather wide limits, without appreciable effect upon either the slope or the half-wave potential of the current–voltage curves. The results of one such test are shown in Table I. For most of our work we have used rates of 10 or 20 millivolts per minute, since these represented an optimum for the operator to read potentials accurately.

TABLE I

EFFECT OF RATE OF APPLICATION OF VOLTAGE ON CURVE CHARACTERISTICS

Rate of applying voltage, millivolt/min.	$E_{1/2}$ vs. S. C. E., millivolts	Slope for log $I/(I_d - I)$ vs. e. m. f., millivolts
0[a]	+12	32.5
10	+11	33.5
20	+11	33
40	+12	33
80	+10	31
160	± 0	37

[a] Application of voltage made in 10-mv. steps. Current reading made after remaining constant for approximately 30 seconds.

With a suitable selection of the galvanometer shunt and of the range of applied voltage, the slidewire motor and recorder-chart motor are started and the current–voltage curve is recorded. A suitable number of electrode potential measurements are made with the potentiometer and recorded at the corresponding "pips" on the current–voltage curve. The half-wave potential is evaluated from the recorder chart and a plot of applied voltage *vs.* the electrode potential. However, from the recorder-chart unit calibration in microamperes, the curves can be replotted in terms of microamperes *vs.* e. m. f. referred to the S. C. E.[10] Two methods are used to evaluate the half-wave potentials from the curves—one based upon the geometric midpoint, and the second based upon the inflection point. These two points have been proved identical by Kolthoff and Lingane,[11] when the curve is symmetrically "S-shaped," as required for a theoretically ideal case. In actual practice, the lower half may be slightly distorted by the accumulation of solid reaction products at the electrode, in which case the determination of the inflection point gives the most reliable results.

Experimental Results

The criteria established for measuring the effectiveness of the dropping mercury electrode as an indicator electrode were used in testing the platinum microelectrode:

(1) A high degree of reproducibility of half-wave potentials is obtained for successive determinations of the same compound. The value of $E_{1/2}$ for a number of determinations for each of several substituted *p*-phenylenediamines is shown in Table II. If four or more curves are used in determining an average value for the half-wave potential, the probable error of that average value seldom exceeds 2 millivolts.

(2) A current–voltage curve is recorded for an increasingly positive or negative applied voltage until a diffusion current is obtained, then the direction of slidewire rotation is reversed, and a record is made with decreasing voltage. For the systems tested, the platinum microelectrode gives, with but few exceptions noted below, good checks between the curves obtained in this manner, as shown in Fig. 1. This simple test has been applied to each new system investigated. A system which does not show identical forward and reverse

TABLE II

PROBABLE ERRORS IN DETERMINATION OF HALF-WAVE POTENTIALS FOR SEVERAL DEVELOPING AGENTS USING Pt MICROELECTRODE

The R_e is probable error of average

Developing agent	*p*H	$E_{1/2}$ vs. S. C. E., millivolts	R_e
p-Aminophenol	11	+129	
		+121	
		+124	
		+121	
	Av.	+124	1.3
4-Amino-N,N-diethylaniline	11	+25	
		+23	
		+27	
		+26	
		+25	
	Av.	+25	0.5
4-Amino-N,N-diethyl-*m*-toluidine	10	+20	
		+19	
		+14	
		+12	
		+18	
		+22	
		+17	
		+17	
		+16	
		+16	
	Av.	+17	0.6
6-Amino-N-ethyl-1,2,3,4-tetrahydroquinoline	10	+33	
		+33	
		+29	
		+36	
	Av.	+33	1.0

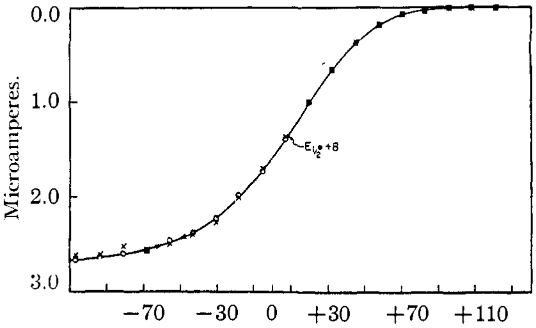

Fig. 1.—Forward and reverse current–voltage curve for 4 - amino - N - ethyl - N-(β - methylsulfonamidoethyl) - *m*-toluidine (5×10^{-4} *M*) + Na_2SO_3 (5×10^{-3} *M*) + 1-phenyl-3-(γ-phenylbutyrylamino)-5-pyrazolone (5×10^{-3} *M*) in diethylglycine buffer (5×10^{-2} *M*) at *p*H of 9.9: O designates data in forward direction; × designates reverse direction.

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[10] The convention for signs of electrode potential used in this paper are those of Lewis and Randall and not those commonly used in polarographic literature.

[11] I. M. Kolthoff and J. J. Lingane, *Chem. Revs.*, **24**, 71 (1939).

curves needs further investigation to determine the cause of the lack of reproducibility. Often material deposited on the electrode changes the diffusion current and thus alters the shape of the reverse curve, as shown in Fig. 2. However, in most of these cases, the half-wave potentials obtained from forward and reverse curves show good agreement. In some cases, notably the hydroquinone–quinone system, the forward and reverse curves do not coincide, as shown in Fig. 3. The curves for the reduction of quinone often show reasonably good reproducibility; however, the same curves for the oxidation of hydroquinone show a pronounced displacement of the half-wave potentials, compared with those for quinone. With the dropping mercury electrode, the half-wave potential for the reduction of quinone, the oxidation of hydroquinone, and the oxidation–reduction of equal molar mixtures of the two are identical. A reason for the anomalous behavior in the case of the platinum microelectrode has been suggested by Müller.[2]

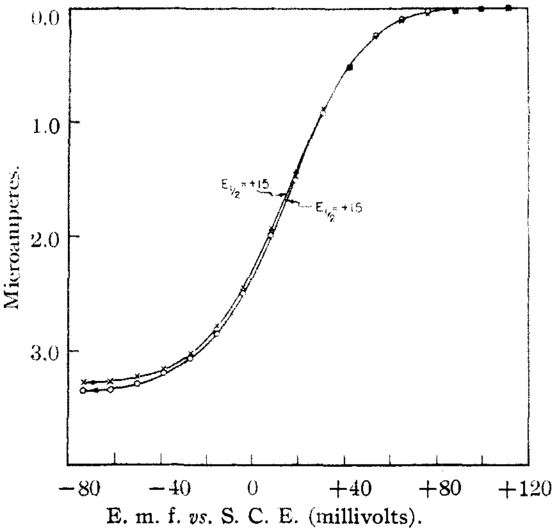

Fig. 2.—Forward and reverse current–voltage curves for 4-amino-N,N-diethyl-*m*-toluidine (5×10^{-4} *M*) in diethylglycine buffer (5×10^{-2} *M*) at *p*H of 9.9: O designates forward direction; X designates reverse direction.

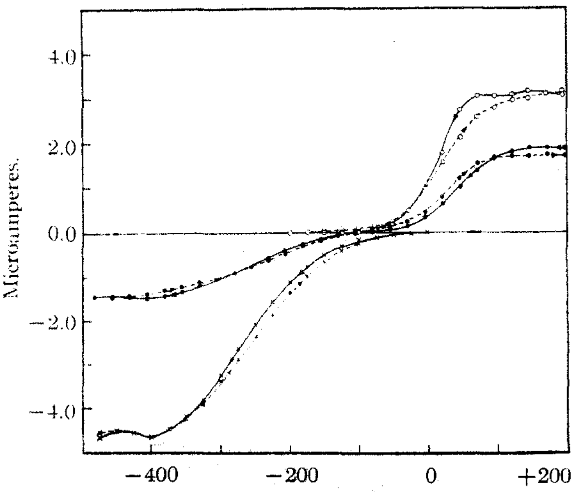

Fig. 3.—Forward and reverse current–voltage curves for hydroquinone–quinone system in diethylglycine buffer (5×10^{-2} *M*): X designates hydroquinone (5×10^{-4} *M*); O designates quinone (5×10^{-4} *M*); and ● designates mixture of hydroquinone and quinone each (2.5×10^{-4} *M*).

(3) The reversibility of a system is tested by comparing the oxidation of the reduced state with the reduction of the oxidized compound. In the case of *p*-phenylenediamines, it is often difficult to measure the reduction of the corresponding diamine, since the latter is unstable in aqueous solution.[12]

(4) An analysis of the current–potential curves by plotting the $\log I/(I_d - I)$ against e. m. f. (mv.) of the electrode, gives a straight line, as was shown to be the case by Müller[13] for systems having theoretically S-shaped curves. Such a plot (for 4-amino-N,N-diethyl-*m*-toluidine at *p*H 10) is shown in Fig. 4 for two different platinum microelectrodes. These values have not been corrected for contribution of the semiquinone, and the resulting slope is too high (40 mv.). A correction for this contribution[14,15] gives the dotted line having a slope of 27 mv., which is close to the theoretical value of 30 mv. None of the other curves in

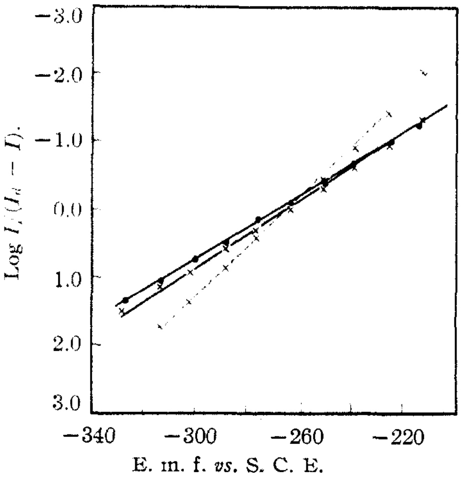

Fig. 4.—Plot of $\log I/(I_d - I)$ *vs.* e. m. f. for 4-amino-N,N-diethyl-*m*-toluidine (5×10^{-4} *M*) in acetate buffer (5×10^{-2} *M*) at *p*H of 4.5, using two different platinum microelectrodes, dotted line for one of the curves corrected for contribution of the semiquinone.

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(12) Recent measurements made on the system, 4-amino-N,N-diethyl-*m*-toluidine, with an automatic recording potentiometer high-speed syringe titrating assembly, in which the total titration was completed in less than two minutes, gave potentials quite similar to those obtained polarographically. At *p*H 10, $E^{\circ\prime} = +19$ and $E_{1/2} = +17$ *vs.* S. C. E. At *p*H 11, $E^{\circ\prime} = +57$ and $E_{1/2} = +56$

(13) O. H. Müller, *J. Chem. Education*, **18**, 227 (1941).

(14) L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 437 (1938).

(15) B. Elema, *Rec. trav. chim.*, **54**, 76 (1935).

the paper have been corrected, since the presence of the semiquinone does not affect the half-wave potential.

(5) A further analysis of the current–voltage curves by the methods of Michaelis[14] and associates, and of Elema,[15] for potentiometric data and adapted to polarographic curves by Müller,[16] indicates a good fit with the theoretical curves. In Fig. 5 such a curve is given for 6-amino-N-ethyl-1,2,3,4-tetrahydroquinoline, which has a large semiquinone constant at pH 4.6. The actual value of the constant was calculated from index potentials by the method of Geake.[17]

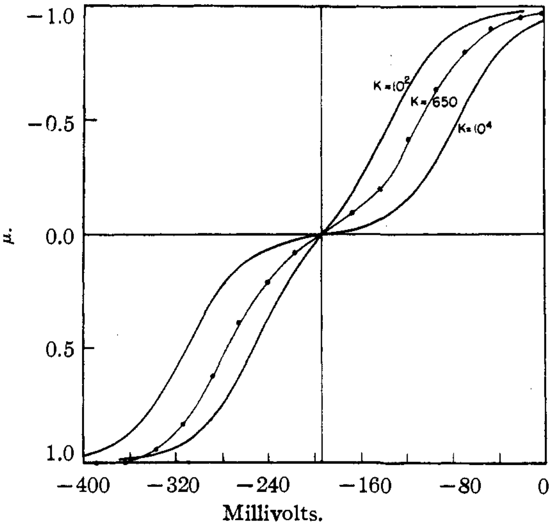

Fig. 5.—Comparison of theoretical and experimental curves for compound having a high semiquinone constant; heavy lines are the theoretical curves for semiquinone constants of 10^2 and 10^4: ● designates experimental data for 6-amino-N-ethyl-1,2,3,4-tetrahydroquinoline (5×10^{-4} M) in acetate buffer (5×10^{-2} M) at a pH of 4.6.

In addition to these checks, a direct comparison was made with the dropping mercury electrode, for certain p-phenylenediamines (and for p-aminophenol), where the half-wave potential is sufficiently positive for using the mercury electrode. Figure 6 (and Fig. 7) show comparison determinations made with Pt and Hg electrodes on the same solutions. Although the curves show minor differences, the resulting half-wave potentials show reasonably close agreement. With but few exceptions, the curves obtained with the two types of electrodes give half-waves differing not more than 3 to 7 millivolts.

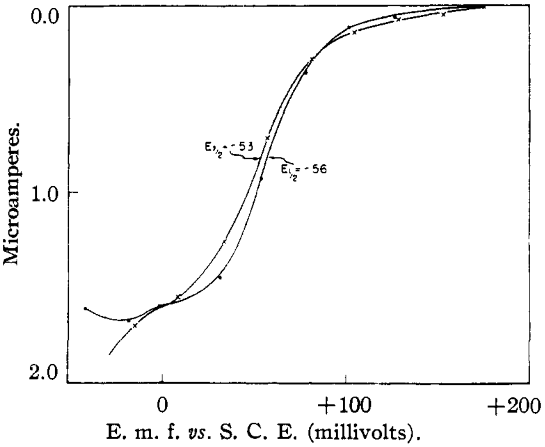

Fig. 6.—Comparison of current-voltage curves obtained with platinum and dropping mercury electrodes for 4-amino-N,N-diethyl-m-toluidine (5×10^{-4} M) in phosphate buffer (5×10^{-2} M) at pH of 11: ● designates platinum electrode; × designates dropping mercury electrode.

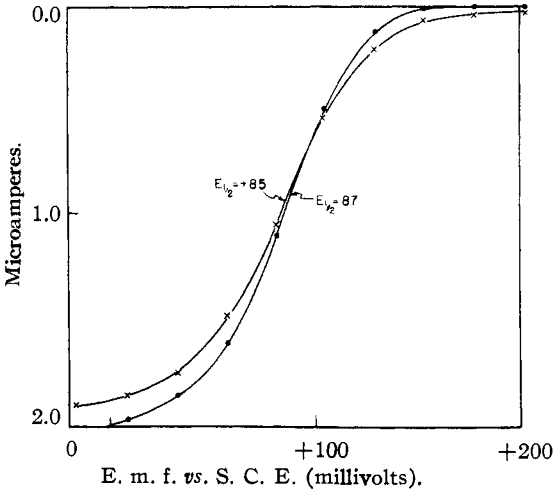

Fig. 7.—Comparison of current-voltage curves obtained with platinum and dropping mercury electrodes for p-aminophenol (5×10^{-4} M) in diethylglycine buffer (5×10^{-2} M) at pH of 10: ● designates dropping mercury electrode; × designates platinum electrode.

Applications.—The use of the half-wave potentials, obtained by the method described, in the study of the effect of structural changes in the distribution of the resonance energy in the developing agents, is illustrated in Table III. In Case I, the addition of a CH_3 group ortho to the free amino group increases the half-wave potential by discrete increments, owing to the electron-releasing ability of the CH_3 group.

In the second example, Case II, the attachment of the substituent on the amino group, to the ring, in order to increase coplanarity, resulted in a large increase in the half-wave potential. The attachment of the second substituent gave an additional and nearly equal increase. On the other hand, the substitution of $—CH_2CH_2NHSO_2CH_3$ for an ethyl group, as in Case III, gave a decrease in the half-wave potential. These and other studies by means of half-wave potentials have been found valuable in an investigation of photographic developing agents, which will be reported in a forthcoming paper from these Laboratories.

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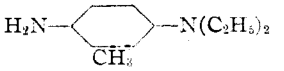
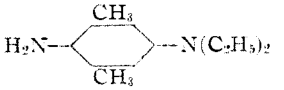
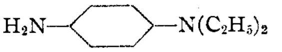
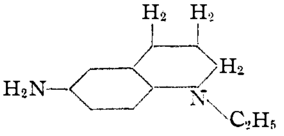
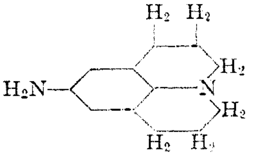
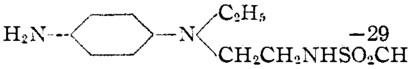
(16) O. H. Müller, *Annals N. Y. Acad. Sci.*, **40**, 91–109 (1940).

(17) A. Geake, *Trans. Faraday Soc.*, **34**, 1395 (1938).

TABLE III

DEVELOPING AGENT (5 × 10^{-4} *M*) IN DIETHYLGLYCINE BUFFER AT *p*H 10.0

Developing agent	$E_{1/2}$ vs. S. C. E. (mv.)	$\Delta E_{1/2}$ (mv.)
CASE I		
	−14	
	+17	+31
	+37	+20
CASE II		
	−14	
	+32	+46
	+73	+41
CASE III		
	−14	
	−29	−15

Acknowledgments.—The authors wish to acknowledge the efforts of A. Weissberger, of the Synthetic Organic Research Department of these Laboratories, in the selection and preparation of the developing agents, and of E. E. Jelley, of these Laboratories, for his interest and coöperation in the development of this method.

Summary

An application of stationary microelectrodes of platinum to the polarographic determination of half-wave potentials has been described. Examples of the anodic oxidation of several phenylenediamines have been given to illustrate the usefulness of the method. The application of the potentials obtained to studies of the effects of variations in the structure of developing agents has been illustrated.

ROCHESTER 4, N. Y. RECEIVED MARCH 1, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography of Copper Complexes. II. Dipyridyl, Orthophenanthroline and Thiourea Complexes. A Double Complex System[1]

BY E. I. ONSTOTT[2] AND H. A. LAITINEN

In this second paper are presented the results of polarographic studies of α,α'-dipyridyl, orthophenanthroline and thiourea, and the combination of ethylenediamine and thiourea as complexing agents for copper(II) and copper(I). Results on ethylenediamine, propylenediamine, diethylenethiamine, and glycine were reported previously.[1]

The copper(II) complexes of dipyridyl and orthophenanthroline are reduced in two steps. In the first step the cupric complex is reduced to the cuprous complex, and in the second step the cuprous complex is further reduced to the amalgam. Other copper(II) complexes which show similar behavior are the ammonia[3,4] pyridine,[5] thiocyanate ion[6] and chloride ion[7] as well as various copper(II) chelates.[8]

Copper(II) complexes of thiourea do not exist; only copper(I) complexes are stable.[9a,b,c,d,e] Hence, a single polarographic wave corresponding to the reduction of a copper(I) complex of thiourea to the amalgam is observed.

Bis-(ethylenediamine)-copper(II) ion in the presence of excess ethylenediamine alone is reduced directly to the amalgam.[1] However, in the presence of a large excess of both ethylenediamine and thiourea, it is reduced first to copper(I) before being further reduced to the amalgam.

Experimental

For the most part, the solutions for analysis were composed from stock solutions of reagent grade chemicals. α,α'-Dipyridyl and orthophenanthroline, obtained from the G. F. Smith Chemical Company, were weighed for each solution prepared, as was the thiourea for solutions requiring a high concentration of this constituent. A stock solution of cupric nitrate was used as the source of copper, except that solutions of the thiourea complex were prepared from a stock solution of cuprous chloride in 0.1 *M* thiourea. The indifferent electrolyte was 0.1 *N* potassium nitrate.

Because of the low solubility of dipyridyl and ortho-

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[1] Paper I, Laitinen, Onstott, Bailar and Swann, THIS JOURNAL, **71**, 1550 (1949).

[2] Abstracted from the Doctorate Thesis of E. I. Onstott, 1950.

[3] Stackelberg and Freybold, *Z. Elektrochem.*, **46**, 120 (1940).

[4] Lingane, *Chem. Rev.*, **29**, 1 (1941).

[5] Lingane and Kerlinger, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 77 (1941).

[6] Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

[7] Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 583 (1943).

[8] Calvin and Bailes, THIS JOURNAL, **68**, 949 (1946).

[9] (a) Kohlschütter, *Ber.*, **36**, 1151 (1903); (b) Kohlschütter and Brittlebank, *Ann.*, **349**, 232 (1906); (c) Rathke, *Ber.*, **17**, 297 (1884); (d) Rosenheim and Loewenstamm, *Z. anorg. Chem.*, **34**, 62 (1903); (e) Walter and Storfer, *Monatsh.*, **55**, 21 (1934).